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DOCTOR OF PHILOSOPHY
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AN IMPROVED DYNAMIC METHOD FOR MEASURING VAPOR PRESSURES

In the study of the colligative properties of solutions use may be made of methods involving the lowering of the freezing point, the lowering of the vapor pressure and the elevation of the boiling point of the solvent by the solute, and the application of electromotive force methods. Because of the ease and the accuracy of the measurements most of the work, hitherto, has been confined to the application of the freezing point and electromotive force methods. Both the freezing point and the boiling point methods are of limited application because of the fact that they can be used accurately only for a narrow temperature interval. The latter method is further handicapped for the reason that we have no accurate specific heat data for liquids at temperatures near their boiling points. While the electromotive force methods may be used at any temperature, they are limited to only those cases for which perfectly reversible electrodes are obtainable.

Of all the properties of solutions none are more accessible to thermodynamic treatment than the vapor pressure. While the method is free from all of the disadvantages of the above mentioned methods and in addition offers many advantages, the results obtained have not been all that could be desired.

Four general methods have been employed for measuring the vapor pressures of solvents and solutions. They are: (1) static, (2) indirect, (3) differential, and (4) dynamic.

The static method has been used by many investigators, including Wüllner[1] and Raoult[2]. In principle, this method consists essentially in placing the liquid whose vapor pressure is to be determined above the mercury in a Torricellian vacuum and comparing the height of the mercury with that in another barometer tube at the same temperature. Tammann[3] has shown, however, that the method is open to serious errors due to small traces of air and volatile impurities unavoidably present in the solution and on the sides of the tubes. Furthermore, there is no assurance that the concentration of the solution remains uniform throughout.

The indirect method, as perfected by Ramsay and Young[4], consists in observing the temperatures at which solutions boil under various pressures. They have used the method extensively and their results on the vapor pressure of water above 100° are still accepted as standard. Emden[5], and Holborn

[1] Wüllner: Pogg. Ann., **103**, 529 (1856); **110**, 564 (1860).
[2] Raoult: Z. physik. Chem., **2**, 353 (1888).
[3] Tammann: Wied. Ann., **33**, 322 (1888).
[4] Ramsay and Young: Phil. Trans., **103A**, 107 (1892).
[5] Emden: Wied. Ann., **31**, 145 (1897).

and Henning[1] have used the method to measure the vapor pressures of many aqueous solutions. The objections to the indirect method are: (1) the liquid and the vapor are both liable to become superheated; (2) in the case of solutions, the concentration is changed by the evaporation of the solvent, and (3) the method is limited by the fact that many solutes decompose on boiling.

The differential method involves the comparison of the vapor pressures of two solutions, or of one solution and the pure solvent, by means of a manometer or a flexible membrane, and it gives directly the vapor pressure lowering. It does not, however, give us any knowledge of the absolute value of the vapor pressure over either liquid phase. Dieterici[2] separated the vapor above two different liquids by a flexible metallic membrane and measured the difference in vapor pressure by the movement of this membrane as magnified by a long pointer. The apparatus is too complicated and inflexible for general application. Fraser and Lovelace[3] have developed a modification of the differential method by which the vapor pressure lowerings may be determined with extreme accuracy. They compare the vapor pressure of a solution with that of the pure solvent by means of a very sensitive Rayleigh manometer. With this apparatus they have been able to measure the vapor pressure lowerings in solutions of potassium chloride, mannite and lithium chloride at 20° with an accuracy of 0.001 mm., or less. The apparatus and its technique require extreme precaution in the preparation of air-free solutions and in keeping them in constant aggitation. The time consumed, which varies from several days to several weeks for a single determination of the vapor pressure lowering, makes the method impractical for any but the most refined work. Tower and Germann[4] have measured vapor pressure lowerings in aqueous and alcoholic solutions by means of a Morley gauge.

The dynamic, or air-saturation method of measuring vapor pressures, is based upon Dalton's Law of partial pressures. The essential features of the method as commonly used are: (1) a measured volume of air is saturated with vapor by passing it over the surface of, or bubbling it through the liquid contained in the saturator, (2) the weight of the solvent evaporated is determined by the loss in weight of the saturator, or by the gain in weight of an absorber which removes the solvent from the effluent air, and (3) the total pressure exerted by the gaseous mixture in contact with the liquid is obtained from barometer and manometer readings. From the data thus obtained the vapor pressure of the liquid may be calculated.

Regnault[5], the first to use the dynamic method, passed air through a flask containing a sponge saturated with the liquid, then through screens of moist silk fastened to frames. The water vapor in the effluent air was determined by absorption in sulphuric acid and subsequent weighing. Since

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[1] Holborn and Henning: Ann. Physik, (4) **26**, 833 (1908).

[2] Dieterici: Wied. Ann., **50**, 47 (1893); Ann. Physik, (4) **70**, 617 (1923).

[3] Fraser, Lovelace, and students: J. Am. Chem. Soc., **38**, 515 (1916); **42**, 1793 (1920); **43**, 102 (1921); **45**, 2930 (1923).

[4] Tower and Germann: J. Am. Chem. Soc., **30**, 1219 (1908); **36**, 2449 (1914).

[5] Regnault: Ann. Chim. Phys., (3) **15**, 129 (1845).

Regnault's time the apparatus employed has undergone many and varied changes. In the modification developed by Ostwald and later used by Walker[1], air is bubbled through two Liebig bulbs containing the solution, then through pure water, and finally through a U-tube containing pumice soaked with sulphuric acid. The air first saturates itself with vapor up to the vapor pressure of the solution and then takes up from the water the quantity of vapor necessary to complete the saturation. Finally, the water is absorbed by sulphuric acid. From the loss in weight of the water bulb, which is proportional to the difference between the vapor pressures of the solution and solvent, and the gain in weight of the acid tube, the relative lowering of the vapor pressure of the solvent is calculated. With slight variations in the apparatus and technique the method has been used with more or less success by a number of investigators.

The Earl of Berkeley and Hartley[2] have concluded that the failure of the original Walker-Ostwald method is due to variations in the hydrostatic pressure in the several vessels. They also suggest that liquid spray is mechanically carried from the solution to the pure solvent. Both of these sources of error were eliminated by passing the air slowly over the surface of the liquid contained in specially designed tubes shaken by the oscillating platform upon which they were mounted. The time required to make a complete vapor pressure determination was about three days and they claim an accuracy of the order of five percent.

Derby, Daniels and Gutsche[3] have determined the vapor pressures of pure alcohol and pure water by passing a measured volume of air axially through two rotating spherical bulbs filled with glass beads and partially filled with the liquid. The volume of air was accurately measured by means of two bulbs, each holding exactly 1135 c.c. The method employed was found to be quite accurate and very rapid. While they usually used from 8 to 10 liters of air for each experiment, they found that as much as 50 liters of air can be passed through the solution in one hour without affecting the efficiency of the saturator or the absorber.

Washburn and Heuse[4] have measured the relative lowering of the vapor pressure for weight molal solutions of cane sugar. They used saturators similar to those used by Berkeley and Hartley, but passed the air in succession through the following train: The air, drawn by a constant level aspirator, passes first through a soda-lime tube and then into the water presaturator, where it is saturated with water vapor at about 50°. The air then passes into a condensation flask which is immersed in the thermostat and here it deposits most of its excess of moisture and enters the first saturator of the train slightly supersaturated. On emerging from this saturator it is in equilibrium with water at 25°. It then passes out of the thermostat through a tube which is

[1] Walker: Z. physik. Chem., **2**, 602 (1888).
[2] Berkeley and Hartley: Proc. Roy. Soc., **77**, 156 (1906).
[3] Derby, Daniels and Gutsche: J. Am. Chem. Soc., **36**, 793 (1914).
[4] Washburn and Heuse: J. Am. Chem. Soc., **37**, 309 (1915).

heated by a coil to about 30°. The warm air then passes at once through an absorber, A_1, where all of the moisture is removed. The perfectly dry air then goes through a second presaturator containing water at 25° where it takes up the bulk of the moisture necessary to bring it into equilibrium with the solution in the saturator, S_2. After passing through this saturator and its absorber, A_2, the perfectly dry air passes directly into the third saturator, S_3, which contains pure water. In the first and third saturators the equilibrium is always approached from opposite directions, thus giving a valuable check upon the experimental conditions. The absorbers are large; about 25 grams of water can be condensed and absorbed in one absorber. Although the apparatus is very large and apparently cumbersome, it is, nevertheless, capable of a high degree of accuracy. In the use of this apparatus the measurement of the volume of air is unnecessary, since the same volume of air passes in turn over the solution and over the solvent, and the weight of the water evaporated from each is determined by the gain in weight of its respective absorber. A single experiment extends over a period of 24 hours, and they claim that the results are accurate to less than 0.5 percent.

A survey of the vapor pressure data obtained by the dynamic method shows not only a wide variation in the values reported by different investigators for a single liquid, but also very frequently a considerable variation in the data given by a single investigator. The chief reasons for these deviations are few, but they have been difficult to overcome. As mentioned before, one of the main sources of error is due to our inability to measure accurately, and at the same time conveniently, the large volume of air required for a single determination. The error thus introduced will be greater or less depending upon the magnitude of the vapor pressure of the liquid studied. This difficulty has been practically eliminated by the method of Washburn and Heuse but the apparatus is almost too cumbersome from the standpoint of convenience and speed. It is also largely eliminated in the method of Derby, Daniels and Gutsche but their apparatus requires constant and immediate attention. Owing to the surface film effect any form of apparatus which requires the passing of air over the surface of the solvent or solution must present a large liquid surface. Moreover, the surface should be in constant motion. Forms of apparatus involving the bubbling of air through the liquid are obviously more compact, but they introduce errors for the reason that while a bubble may be saturated with the vapor in the depth of the liquid, it will expand on rising and may become unsaturated. Unless, therefore, the air passes over the surface of the liquid again it may leave the apparatus without becoming entirely saturated. Again the mathematical formulae which have been used, heretofore, have been complicated; slight errors of observation are highly magnified in calculating vapor pressures.

In the pages which follow we shall describe an apparatus and its technique which greatly improves the dynamic method and eliminates many if not all of the difficulties experienced in the past

Apparatus

To reduce the errors involved in measuring the large volume of gas passed through the liquid we have generated the gas electrolytically and we are able to calculate indirectly from the mass of silver deposited in the coulometer not only the actual volume of the gas, but also the total number of mols of hydrogen and oxygen. The final form of the apparatus is shown in Fig. 1. Six electrolytic gas cells, A, are connected in series through the silver coulometer,

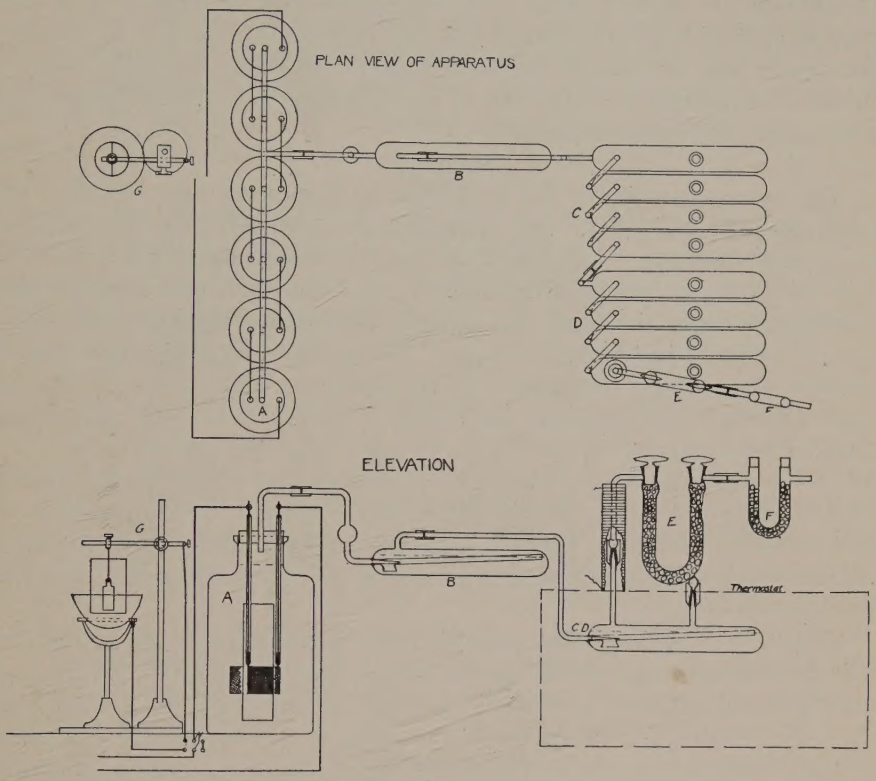

FIG. 1

S, with the laboratory storage battery system. The gases generated pass through a manifold tube into the presaturator, B, maintained at a few degrees higher than the bath temperature. From B the gases pass to the saturator, C, consisting of a battery of four saturation tubes sealed in series and containing pure conductivity water. In this way the moisture content of the gas is reduced to the normal saturation pressure at the temperature of the experiment. The gas then passes to a bank of four similar absorbers, D, containing the solution under investigation, where the vapor pressure falls to the normal vapor pressure of the solvent over the solution. Both C and D are immersed in a large Freas water thermostat maintained at 25° ± 0.002. Finally, the saturated gases pass through the absorber, E, and the protection tube, F, to the atmosphere.

Generators

The generators were wide mouth glass bottles of three and one-half liters capacity, each filled to the neck with a 25 percent solution of sodium hydroxide. The electrodes were of nickel wire gauze, each 3.5 by 9 inches, suspended by heavy nickel wire leads. The leads were inclosed by glass tubes passing through the rubber stopper. The tubes were fused to the wire at the bottom for a length of one inch, filled with melted paraffin and then sealed at the top with sealing wax to prevent leaks. The electrodes were separated by a glass cylinder extending through the middle two-thirds of the depth of the solution, thus preventing any possible recombination of the gases due to the catalytic influence of the nickel. The top of each electrolytic cell was hermetically sealed with De Khotinsky cement.

Saturators

The saturators were of the type used by Bichowsky and Storch[1]. The gases enter the bulb (Fig. 1. B) through a short central tube tapered down to a 2 mm. capillary. At the tip of the capillary the stream of gas breaks into bubbles which pass up a slightly inclined 5 mm. tube 10 inches long and then break at the end of the tube. An opening is blown through the lower side of this inclined tube just back of the tip of the capillary. Through this opening liquid is drawn from the bottom of the saturator and carried by the gas bubbles up the slanting tube to the surface of the liquid, thereby maintaining a practically uniform vapor concentration. The gas liberated from the bubbles as they burst then passes back over the surface of the liquid to an orifice leading either to a second saturator, or, finally, to the absorber, E. Each tube in a saturator, C or D, is provided with a vertical tube for filling and emptying. When the saturators are in use these tubes are closed by mercury seal stoppers.

This type of saturator has three distinct advantages over the Liebig bulb and the ordinary wash bottle type of saturators. They are: (1) each bulb introduces only a small hydrostatic pressure (about 1/2 inch of water), (2) after this pressure is released by the breaking of the bubble, the gas passes for some distance over the surface of the liquid, thereby having opportunity to come into equilibrium with the latter, and (3) the liquid is more efficiently stirred.

Absorber

The absorber consists of a six inch glass-stoppered U-tube joined by means of a mercury seal to the last bulb of the saturator D. The absorber contains glass beads which have been thickly coated with phosphorus pentoxide by rotating the beads in a bottle containing the oxide. This type of absorber exposes a large surface to the gases without offering any appreciable resistance to the flow. The protection tube F also contains beads similarly coated; this prevents moisture diffusing into the absorber from the atmosphere.

The silver coulometer used was of the porous cup type. The specifications proposed by Rosa and Vinal[2] were minutely followed. The electrodes were

[1] Bichowsky and Storch: J. Am. Chem. Soc., **37**, 2696 (1915).
[2] Rosa and Vinal: Bull. Bureau of Standards, **13**, 497 (1917).

supported by heavy glass rods set in iron stands. The anode was cast in the form of a cylinder from pure silver; the cathode was a platinum dish of 250 to 300 c.c. capacity. The porous cup was soaked in dilute nitric acid for several days, then distilled water was filtered through it, and it was finally heated at 130° to remove the last traces of acid. A solution of 15 grams of silver nitrate in 100 c.c. of water was used for the electrolyte.

The temperature of the bath was read from a normal glass thermometer, (B. S. No. 21577); the smaller fluctuations in temperature were indicated by means of a Beckmann thermometer immersed at the same point in the bath. Barometric pressures were read from a large precision barometer, readable by vernier to 0.05 mm. All pressures were reduced to 0°, sea level and 45° latitude.

Materials

Mannite. Pfanstiehl's "C. P." mannite was further purified according to the method of Brahme[1]. It was twice precipitated from distilled water and once from conductivity water by the addition of alcohol. After a second recrystallization it melted sharply at 166°. It was then dried and heated to constant weight at 125°-130°.

Potassium Chloride. A good "C. P." sample of the salt was twice recrystallized from pure distilled water and once from conductivity water. After drying, the salt was heated in a platinum dish until decrepitation ceased and then preserved in a desiccator over P_2O_5 until used.

Silver. The silver used as anodes was specially prepared and the analysis showed that it was 99.8 percent pure. It was further purified by electrolysis, then fused and cast in the form of cylinders. Chemically pure silver nitrate was twice recrystallized from dilute nitric acid solution and then repeatedly fused with excess nitric acid to remove organic impurities.

The various molal solutions of potassium chloride and mannite were made with water distilled from an alkaline permanganate solution and condensed in a block tin condenser.

Experimental

In order to avoid the evaporation and condensation of any solvent on the walls of the tube leading from the solution saturator, the current was turned through the coil surrounding the mercury seal. At the same time the direct current was switched through the electrolytic cells and gas was passed through the saturators for about one-half hour before the coulometer or the absorber were attached.

The absorber, E, was counterpoised on a sensitive balance by a similar U-tube filled with glass beads. After coming to equilibrium, one stopper of each tube was temporarily opened and the final weighing was made. A platinum dish cathode, previously cleaned, dried at 150° and cooled in a desiccator, was accurately weighed. All weighings were made by the oscillation method and are accurate to ±0.01 mg. At the end of the half hour period the switch to the generator was opened, the coulometer assembled,

[1] Brahme: J. Am. Chem. Soc., 41, 1707 (1919).

and the absorber and protection tube were put in place. The current was immediately switched through the whole system and the barometer reading was taken. Barometer readings were taken at frequent intervals throughout the experiment. At the end of the experiment the current was shut off and the absorber and protection tube were connected by another mercury seal to a long glass tube containing beads coated with P_2O_5, An aspirator was attached to F and dry air was drawn through the absorber to displace the gaseous mixture of hydrogen and oxygen, and to carry any vapor condensed on the side arm of the absorber into the absorber itself. Aspiration was continued for an hour, after which the absorber was removed, closed, wiped with clean dry chamois skin, and then allowed to stand in the tightly closed balance case over night. The final weighings were made with one stopcock open. Repeated aspiration of the absorber with dry air did not measurably change the final weight. At the completion of the experiment the electrolyte was siphoned from the platinum dish and the deposit was washed free from silver nitrate. The dish was then dried for an hour at 150°, cooled in a desiccator and weighed.

From the three data thus obtained, viz., the weight of the water evaporated, W_w, the weight of the silver deposited, W_s, and the corrected barometer pressure, P, the vapor pressure of the solution can be easily calculated by a direct application of Dalton's law. Thus, if the mixture of hydrogen, oxygen and water vapor are in equilibrium with the solution at the atmospheric pressure, P, (corr.), then the partial pressure of the water vapor, p, in the mixture will be proportional to its mol fraction. That is,

$$p = \frac{n_1}{n_1 + n_2} P,$$

where n_1 is the number of mols of water vapor and n_2 is the number of mols of hydrogen and oxygen combined. n_1 is calculated from the weight of water vapor collected in the absorber and the molecular weight of water, thus $n_1 = W_w/18.016$. n_2 is obtained from the weight of silver deposited in the coulometer. While the electrochemical reaction:

$$2\,Ag^+ + 2\,(e) \longrightarrow 2\,Ag\,,$$

is taking place at the coulometer cathode six mols of hydrogen and three mols of oxygen are being liberated in the six generators, or nine mols of gas for every two equivalents of silver deposited. Therefore,

$$n_2 = W_s/2 \times \frac{107.88}{9} = \frac{W_s}{23.9733}.$$

In the final form the expression for vapor pressure reduces to

$$p = \frac{\frac{W_w}{18.016}}{\frac{W_w}{18.016} + \frac{W_s}{23.9733}} \times P.$$

For example, let us assume the data from the first experiment in Table I. Here, W_s = 16.5944 g. Ag, W_w = 0.41325 g. water, and P = 740.43 mm. The value of p, the vapor pressure of water at 25°, is found to be 23.7496 mm.

The simplicity of this method of calculating vapor pressures is apparent. It is only necessary to know three experimental values,—the corrected barometric pressure, and the weight, W_w, of water collected in the absorber while W_s grams of silver are being deposited in the coulometer. This indirect method of measuring the volume of gas passed through the liquid is unquestionably more accurate than any method used heretofore. Furthermore, the simple mol fraction equation, p = xP, used in the calculation does away with the complicated equations, and their many uncertain constants, required in other dynamic methods. The only point about which a question may be raised is the assumption of the validity of Dalton's law. In a sense, this method reduces vapor pressures to the same basis as that used in calculating atomic weights, viz., Ag = 107.88.

Application of the Method to Aqueous Solutions

As a test of the accuracy and duplication attainable we have applied the method to the measurement of the vapor pressures of pure water and aqueous solutions of potassium chloride and mannite. The results are collected in Tables I-IV. These are self-explanatory.

TABLE I

Vapor Pressure of Water at 25°

W_s Ag g.	W_w H_2O g.	n_2 H_2+O_2 mols.	n_1 H_2O mols.	n_1+n_2 Total mols.	P (corr.) mm.	p Vapor mm.
16.5944	0.41326	0.69220	0.02294	0.71514	740.43	23.749
14.2969	0.35760	0.59636	0.01985	0.61621	737.48	23.756
15.6673	0.39485	0.65353	0.02192	0.67545	731.87	23.747
15.0538	0.37212	0.62794	0.02065	0.64859	745.92	23.754
16.8377	0.42192	0.70255	0.02342	0.72577	735.86	23.745
14.6417	0.36258	0.61075	0.02012	0.63087	744.68	23.756
18.2425	0.45635	0.76095	0.02533	0.78628	737.37	23.754
16.9104	0.42010	0.70538	0.02332	0.72870	742.23	23.751
					Mean	23.752

The results thus obtained for water vapor show better agreement among themselves than those generally obtained by dynamic methods, heretofore. In only one case is the deviation from the mean as great as 0.007 mm. Also, the mean value, 23.752 mm., is identically the same as that obtained by Derby, Daniels and Gutsche[1], and it agrees favorably with the other values for the vapor pressure of water found in the literature. The following values have been obtained by other investigators at 25°.

[1] Derby, Daniels and Gutsche: J. Am. Chem. Soc., **38**, 793 (1914).

TABLE II

Vapor Pressure of Aqueous Solutions of Potassium Chloride at 25°.

M.	W_s Ag g.	W_w H_2O g.	n_2 H_2+O_2 mol	n_1 H_2O mol	P corr. mm.	p mm.	p mean mm.	p_o-p mm.	$\frac{p_o-p}{M}$
0.20	17.7227	0.44080	0.73926	0.02446	736.45	23.593			
	16.4055	0.40800	0.68432	0.02265	736.37	23.588			
	18.4370	0.45800	0.76906	0.02542	737.88	23.611	23.597	0.155	0.775
0.40	21.3610	0.52467	0.89103	0.02912	740.82	23.447			
	20.9742	0.51767	0.87489	0.02873	737.49	23.451			
	14.1376	0.34583	0.58972	0.01919	743.68	23.445	23.448	0.304	0.760
0.60	16.7350	0.40886	0.69806	0.02269	740.07	23.302			
	14.6971	0.35770	0.61306	0.01985	742.40	23.289			
	15.5702	0.37712	0.64948	0.02096	745.04	23.298	23.296	0.456	0.760
0.80	13.9353	0.34218	0.58128	0.01899	732.89	23.189			
	14.4390	0.35260	0.60229	0.01957	734.65	23.121			
	13.7586	0.33048	0.57391	0.01834	746.66	23.126			
	12.3099	0.29698	0.51348	0.01648	743.63	23.130			
	16.8350	0.41001	0.70224	0.02276	738.38	23.178			
	16.2922	0.39643	0.67959	0.02200	737.32	23.125			
	18.7112	0.44995	0.78050	0.02497	747.67	23.182			
	17.5324	0.42158	0.73133	0.02340	747.98	23.191	23.15	0.597	0.745
1.00	17.5576	0.42222	0.73238	0.02343	742.96	23.037			
	16.9542	0.40991	0.70721	0.02269	739.16	22.985			
	14.9746	0.36141	0.62463	0.02006	740.09	23.029	23.017	0.735	0.735

Table II (continued)

1.50	17.0601	0.40410	0.71163	0.02243	750.54	22.628			
	15.9783	0.37561	0.66650	0.02084	745.58	22.615			
	16.3163	0.38703	0.68060	0.02148	739.13	22.616	22.620	1.132	0.755
2.00	13.7540	0.31966	0.57372	0.01772	741.25	22.237			
	13.0884	0.30403	0.54595	0.01687	741.79	22.241			
	14.5530	0.33866	0.60704	0.01879	740.78	22.250	22.243	1.509	0.754
2.50	21.5220	0.49205	0.89774	0.02731	741.60	21.895			
	13.8685	0.31919	0.57849	0.01772	736.52	21.886			
	13.9650	0.32343	0.58252	0.01795	730.86	21.851	21.877	1.875	0.750
3.00	12.9575	0.29563	0.54049	0.01641	728.77	21.473			
	14.9132	0.33816	0.62207	0.01877	734.07	21.501			
	20.2510	0.45407	0.84473	0.02520	742.72	21.518	21.497	2.255	0.751
3.50	17.2996	0.37800	0.72162	0.02098	747.07	21.108			
	15.9324	0.34842	0.66549	0.01934	745.85	21.090			
	18.7850	0.41392	0.78358	0.02297	739.79	21.068	21.089	2.663	0.761
4.00	19.8143	0.42702	0.82651	0.02370	743.47	20.726			
	18.5494	0.39892	0.77375	0.02214	743.33	20.680			
	18.6468	0.40143	0.77781	0.02228	743.77	20.713			
	20.4302	0.43877	0.85220	0.02435	743.70	20.663	20.696	3.056	0.764
4.81	18.6775	0.38852	0.77909	0.02156	742.27	19.993			
	15.6524	0.32656	0.65291	0.01813	742.12	20.047			
sat'd.	18.0159	0.67470	0.75149	0.02080	742.33	19.991			
	12.0848	0.25118	0.50409	0.01394	745.05	20.052	20.021	3.731	0.776

Observer	Method	p_{25}
Regnault[1]	Dynamic	23.55 mm.
Lincoln and Klein[2]	Dynamic	23.76
Holborn and Henning[3]	Static	23.69
Eckholm[4]	Interpolation formula	23.79
Scheel and Heuse[5]	Static	23.76
Krauskopf[6]	Dynamic	23.71
Derby and Daniels[7]	Dynamic	23.75
Pearce and Snow	Dynamic	23.752

The complete data for the vapor pressures of aqueous solutions of potassium chloride are given in Table II. In this we have included all of the data obtained for each concentration of the salt, and we have simply taken the mean values without rejecting those values which appear to be in error. In some cases the agreement between the values for any one concentration is less than one might desire, and less, also, than the accuracy of which the method is capable. The vapor pressure values for the various solutions, however, are in general more consistent than those obtained by other modifications of the dynamic method. Most of the data presented was obtained during the extreme heat of the summer session. The deviations observed are due almost entirely to difficulties in controlling the temperature conditions accurately over a period of several hours. Under ideal conditions there is no reason why the accuracy obtainable should not approach that of the silver coulometer itself.

The values for the molal lowering of the vapor pressure are given in the last column. While they show considerable irregularity, they show also the same general trend as those calculated by Fraser, Lovelace and Sease[8], using their very accurate differential method. They have found that the curve for the plot of the molecular lowering of the vapor pressure, $(p_o - p)/m$, against the molar concentration passes through a distinct minimum at about 1.0 m, with a slight irregular hump in the curve between 0.4 m and 0.8 m. A rough plot of similar data obtained by our apparatus also shows a minimum in the molal lowering of the vapor pressure at 1.0 M, but the hump has its maximum in the neighborhood of 1.5 M. While there is undoubtedly a minimum value, the average value for the molal lowering for the twelve concentrations studied is 0.7572 mm. At no concentration does the deviation from this value exceed ± 0.02 mm., a value which could easily be accounted for by an error of 0.02 mm. to 0.03 mm. in the vapor pressure reading.

To test the efficiency of the apparatus further we have measured the vapor pressures of four aqueous solutions of mannite. The results obtained are given in Table III.

[1] Regnault: Ann. Chim. Phys., (3) **15**, 129 (1845).
[2] Lincoln and Klein: J. Phys. Chem., **11**, 318 (1907).
[3] Holborn and Hoenning: Ann. Physik, (4) **26**, 833 (1908).
[4] Eckholm: Arkiv. Math. Astr. Phys., **4**, 29 (1908).
[5] Scheel and Heuse: Ann. Physik, (4) **31**, 715 (1910).
[6] Krauskopf: J. Phys. Chem., **14**, 489 (1910).
[7] Derby and Daniels: J. Am. Chem. Soc., **38**, 793 (1914).
[8] Fraser, Lovelace and Sease: J. Am. Chem. Soc., **43**, 106 (1921).

TABLE III

Vapor Pressures of Mannite Solutions at 25°

M	W_s Ag g.	W_w H_2O g.	n_2 H_2+O_2	n_1 H_2O	P corr. mm.	p mm.	p mean mm.
0.4	27.9611	0.69045	1.16634	0.03832	741.53	23.590	
	18.5629	0.45535	0.77431	0.02527	745.95	23.579	
	21.4427	0.52757	0.89444	0.02928	744.08	23.588	23.586
0.6	18.9621	0.46340	0.79096	0.02572	745.80	23.489	
	16.5346	0.40452	0.68971	0.02245	745.44	23.503	
	16.0165	0.39180	0.66809	0.02175	744.64	23.475	
	18.7486	0.45880	0.78206	0.02546	746.10	23.529	
	18.3812	0.45037	0.76673	0.02499	744.48	23.506	
	15.8026	0.38792	0.65917	0.02153	742.76	23.495	23.499
0.8	18.5624	0.45638	0.77429	0.02533	738.83	23.406	
	15.9094	0.39143	0.66363	0.02173	738.99	23.427	
	18.5963	0.45709	0.77571	0.02537	739.20	23.412	23.415
1.0	13.7688	0.33604	0.57434	0.01865	741.92	23.337	
	17.3198	0.41907	0.71830	0.02326	743.41	23.319	
	20.0870	0.49080	0.83789	0.02724	740.82	23.328	23.326

The values for the vapor pressure of the solvent for the two series of solutions are graphically shown in Fig. 2. The extreme smoothness of the curves and the fact that the points fall so nearly upon a straight line speak for the accuracy obtainable by the method. The curve for mannite is a straight line throughout. For potassium chloride solutions up to 3.5 M the maximum displacement from the straight line curve does not exceed 0.02 mm., and at 4.8 M the deviation is only 0.10 mm. The striking apparent proportionality between the vapor pressure lowering, $p_o - p$, and the molality for solutions of potassium chloride up to 0.6 M is shown in Fig. 3. Within limits of experimental error the curve for mannite solutions is a straight line, as we should expect.

TABLE IV

Observed and Calculated Vapor Pressure Lowering produced by Mannite at 25°

M	X mol fract.	P mm.	$p_o - p$ obs. mm.	$p_o - p$ calc. mm.	$\frac{p_o - p}{M}$ mm.
0.0	0.000000	23.752	0.000	0.000	
0.4	0.007155	23.586	0.166	0.169	0.415
0.6	0.010694	23.499	0.252	0.254	0.420
0.8	0.014208	23.415	0.337	0.3375	0.421
1.0	0.017697	23.328	0.424	0.420	0.420

According to Raoult's law the lowering of the vapor pressure of a solvent is directly proportional to the mol fraction, x, of the solute. For comparison, the observed values for $p_o - p$ for mannite solutions and those calculated from Raoult's law are given in Table IV. The last column contains the calculated values for the molal lowering of the vapor pressure produced by mannite. In both cases the agreement is satisfactory.

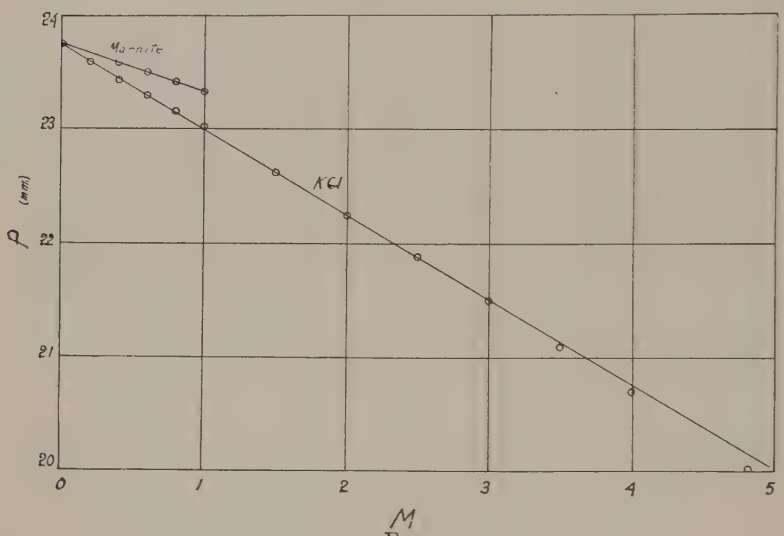

FIG. 2

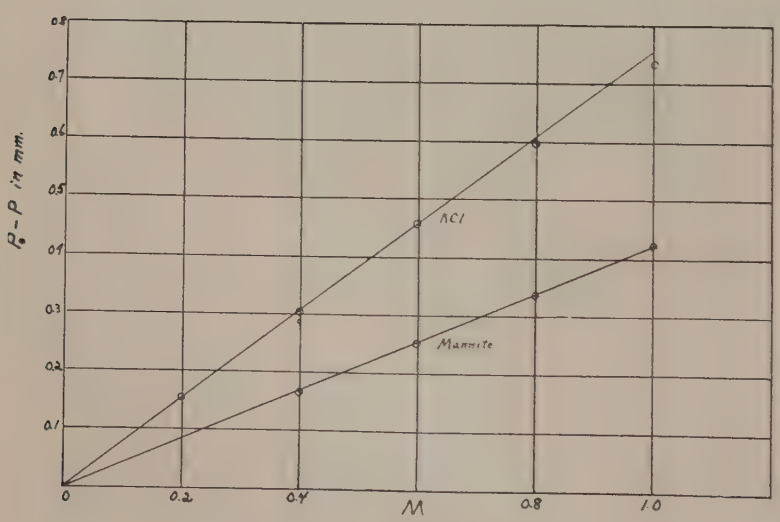

FIG. 3

Summary

1. A new modification of the dynamic method of measuring vapor pressures has been developed.

2. The method introduces the following new features. Instead of measuring the volume of air which passes through the solution, hydrogen and oxygen are generated electrolytically, and the volume of the mixed gases, as well as the number of mols of each, is calculated from the weight of silver deposited in a coulometer.

3. The actual calculation of the vapor pressure requires the knowledge of three single values, viz., the corrected barometric pressure, P, and the weight of the vapor, W_w, taken up by the absorber while W_s grams of silver are being deposited in the coulometer. The number of mols of water vapor, n_1, and the total number of mols of hydrogen and oxygen, n_2 are calculated from W_w and W_s, respectively. From this data the vapor pressure of the solvent is calculated by means of the simple equation,

$$p = \frac{n_1}{n_1 + n_2} P.$$

4. The method has been applied to the determination of the vapor pressures of pure water and aqueous solutions of potassium chloride and mannite at 25°*.

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* The method is being extended to the determination of the vapor pressure of aqueous solutions up to the limits of solubility.

BIOGRAPHY

Robert Dewey Snow was born in Le Claire, Iowa, February 13, 1899. His early education was obtained in the public schools of that town. He entered the State University of Iowa in 1919 and graduated in 1923 with the degree of Bachelor of Science in Chemical Engineering.

In 1923, he received a scholarship from the Graduate College and pursued graduate work in Chemical Engineering. He received the Master of Science degree in 1924. During the years 1924-1926, he was graduate assistant in chemistry.

He is a member of Gamma Alpha, Sigma Xi, Tau Beta Pi, and Phi Lambda Upsilon.